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(19)

(54) CATALYTIC HYDROGEN CONTACT PROCESS

(71) We, TEXACO DEVELOPMENT CORPORATION, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of 135 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a hydrocarbon hydroconversion process and includes the catalytic desulfurization of heavy hydrocarbon materials and the catalytic hydrocracking of heavy hydrocarbon materials. It is more particularly concerned with a process wherein increased sulfur reduction and increased yields of lower-boiling hydrocarbons and selectivity of the yields of lower-boiling hydrocarbons within a particularly preferred boiling range may be obtained.

Catalytic treatment of heavy hydrocarbon materials at temperatures in the range of 500 to 850°F and elevated pressures in the presence of hydrogen to effect hydrocracking is known in the prior art. In general, prior-art hydrocracking practice involves heating a heavy hydrocarbon material to the desired reaction temperature and mixing therewith, either before or after heating, the desired amount of hydrogen and then passing the mixture into the upper portion of a reactor or reactor section containing a bed of granular catalytic material. In the reactor, a liquid phase which is composed of the higher hydrocarbons from the feed containing dissolved or absorbed hydrogen passes downwardly through the reactor in contact with the catalyst together with the downflowing stream of hydrogen (e.g. a downflow process). Alternatively, the liquid feed can be introduced near the top and the hydrogen introduced near the bottom of the reactor and the vapor phase portion of the feed stream, together with stripping hydrogen and hydrogen liberated from the feed stream, can move upwardly through the upper portion of the reactor (countercurrent gas-liquid flow process).

A hydrodesulfurization process which has been proposed heretofore is to introduce a mixture of hydrogen and a wide-boiling-range hydrocarbon fraction into a reaction vessel containing a hydrodesulfurization catalyst at an intermediate point in the vessel, the mixture being preheated to the temperature at which the hydrodesulfurization reaction is carried out, so that the phase-separation takes place at the point of introduction of the reactants. The gas phase, composed mostly of hydrogen and low-boiling hydrocarbons from the feed flows upwardly through the reactor into contact with a suitable catalyst in such manner that vapor-phase conversion is carried out in the total absence of any liquid, at the same time, the liquid phase composed largely of hydrocarbons in the higher boiling ranges containing dissolved hydrogen passes downwardly in the reactor over the catalyst contained therein. This process can be referred to as a split-flow hydrodesulfurization process.

It is possible by this invention to improve the efficiency of such split-flow hydrodesulfurization process.

It is also possible by this invention to provide a split-flow hydroconversion process wherein increased yields of desired lower-boiling hydrocarbons are obtained from the hydrocracking of heavy hydrocarbon materials. Substantially complete conversion to lower-boiling hydrocarbons may be obtained.

It has now been found that desulfurization of heavy hydrocarbon materials and hydrocracking of heavy hydrocarbon materials can be accomplished in a split-flow hydrogen contact process which comprises introducing a heavy hydrocarbon charge stock in downward flow into a catalyst zone in which the reaction conditions include a temperature of from 600 to 850°F and a pressure of from 500 to 5000 psig, said catalyst zone comprising a first catalyst zone below and a second catalyst zone

above the point of entry of the heavy hydrocarbon charge stock, introducing hydrogen into said first catalyst zone in countercurrent relationship to said heavy hydrocarbon charge stock, in order to maintain a lower-boiling liquid in the second catalyst zone and recovering lower-boiling liquids derived from the charge stock from the second catalyst zone under hydrocracking conditions of temperature, pressure and space velocity and hydrocarbons of reduced sulfur content from the first and second catalyst zones under hydrodesulfurization conditions of temperature, pressure and space velocity. It is a critical aspect of this invention that lower-boiling liquid (hereinafter sometimes referred to as liquid) be maintained in the second catalyst zone. It has been found that when liquid is maintained in the second catalyst zone above the point of entry of the heavy hydrocarbon charge stock, increased hydrodesulfurization occurs under hydrodesulfurization process conditions and increased conversion and selectivity in such conversion to lower-boiling hydrocarbons within a particularly preferred boiling range to lower-boiling hydrocarbons are obtained under hydrocracking conditions of pressure, temperature and space velocity.

It has been found that when a lower-boiling liquid is maintained in the second catalyst zone and the effluent from the first catalyst zone is recycled to the heavy hydrocarbon charge stock, substantially complete conversion of the heavy hydrocarbon charge stock to lower-boiling liquids is accomplished. In addition the conversion to lower-boiling hydrocarbons is accomplished with selectivity in such conversion to lower-boiling hydrocarbons which boil within a particularly preferred boiling range. Thus, the amount of gaseous products such as methane and ethane which are formed is small in comparison to the selective yield of more of preferred lower-boiling hydrocarbons. In addition, it has been found that the substantially complete conversion of a heavy hydrocarbon charge stock to lower-boiling hydrocarbons does not result in any substantial build-up in the first catalyst zone of hydrocarbon materials boiling above 850°F thus permitting substantially complete conversion and selectivity in such conversion of the charge stock to lower-boiling hydrocarbons on a continuous basis. In general, conversion of a charge stock to hydrocarbons boiling below 850°F of at least 90% more preferably above 95% and still more preferably above 99% on a weight basis are obtained on a continuous basis. The recycle feature of this invention in addition provides, quite unexpectedly, a process which has low frequency of catalyst regeneration, low hydrogen consumption and substantial hydrocracking conversion at low hydrocracking temperatures.

In carrying out the process of this invention, the heavy hydrocarbon charge stock is introduced into a catalyst zone herein defined to include a first catalyst zone below the point of entry of the the heavy hydrocarbon charge stock and a second catalyst zone above the point of entry of the heavy hydrocarbon charge stock. By the use of the term "above" in reference to the second catalyst zone is meant only that the second catalyst zone is in upflow relationship to the flow of the hydrogen containing gas and in upflow relationship to the volatile hydrocarbon and entrained liquid hydrocarbon which proceed from the first catalyst zone into a second catalyst zone. The word "above" is used to define a flow relationship with the first catalyst zone, which relationship provides for the flow of hydrogen, volatile hydrocarbons and entrained lower boiling liquid hydrocarbons from the first catalyst zone in countercurrent relationship with the downward flow of the heavy hydrocarbon charge stock into a second catalyst zone. Thus the second catalyst zone can be located directly in a space dimensional sense above the first catalyst zone as when the first and second catalyst zone are present in a vertical reactor with an intermediate point of entry for the heavy hydrocarbon charge stock. However this invention contemplates that the second catalyst zone can be present as a separate reactor which is connected to the first reactor by conduit means although it is preferred in carrying out the process of this invention to use a vertical reactor wherein the first catalyst zone and second catalyst zone are present in the same reactor. Within the first and second catalyst zone is present a catalyst which has either hydrodesulfurization, hydrocracking or a combination of both activities under process conditions of temperature, pressure and space velocity which are utilized during the process. In addition, the catalyst in the first catalyst zone can be either the same as or different from the catalyst present in the second catalyst zone. Thus, for example, the catalysts when different can be different hydrodesulfurization, different hydrocracking catalysts or a one of each of a hydrodesulfurization and a hydrocracking catalyst.

The heavy hydrocarbon charge stock upon entry to the catalyst zone proceeds in downflow relationship to the first catalyst zone. Hydrogen is introduced into the first catalyst zone at the lower extremity and/or at intermediate points in said first catalyst zone in countercurrent relationship to the first catalyst zone and in upflow relationship to the volatile hydrocarbons and entrained liquid hydrocarbons which proceed into the second catalyst zone. The volatile hydrocarbons and the liquid hydrocarbons which are present in the second catalyst zone proceed from the second catalyst zone usually in a volatile state and are recovered by conventional means such as by cooling of the hydrocarbon vapors and liquid. The hydrogen which proceeds from the second catalyst zone can then be recycled together with fresh hydrogen

into the first catalyst zone. In addition, hydrogen optionally can be blended with the heavy hydrocarbon charge stock and such charge stock can be introduced at ambient temperature or higher such as temperatures up to hydrodesulfurization or hydrocracking temperatures into the catalyst zone. As stated above, it is a critical aspect of this invention that liquid be maintained in the second catalyst zone. In general, a liquid is maintained in the second catalyst zone by the rate of introduction of hydrogen into the first catalyst zone by any of the means set forth above for the introduction of hydrogen. In order to maintain liquid in the second catalyst zone utilizing hydrogen, it has been found that hydrogen rates of at least 3000 SCF per barrel of liquid feed (505 normal m^3 per m^3 of feed measured at 0°C), preferably from 3000 SCF per barrel of liquid feed up to about 25,000 SCF per barrel of liquid feed (4210 normal m^3 per m^3 of feed measured at 0°C) are required in the first catalyst zone. The hydrogen need not be pure and gases containing more than about 65 volume percent hydrogen may be used. In this connection, the term "hydrogen" is also intended to include dilute hydrogen, reformer by-product hydrogen, hydrogen produced by the partial oxidation of hydrocarbon materials followed by shift conversion and electrolytic hydrogen. Thus hydrogen gas streams such as from catalytic reforming units wherein the hydrogen-containing off-gas from the reforming unit will contain impurities such as methane and ethane are satisfactory. The rates set forth above pertain to the actual hydrogen gas rates which are introduced into the first catalyst zone to maintain liquid presence in the second catalyst zone.

The hold-up of the liquid hydrocarbon charge stock in the first catalyst zone can be varied somewhat by varying the upward flow of hydrogen. In general, it is preferred to have high liquid hold-up, that is a hold-up of hydrocarbon charge stock which provides for maximum catalytic effectiveness for the conversion of the charge stock to lower-boiling hydrocarbons.

The liquid which is maintained in the second catalyst zone in general is derived from the heavy hydrocarbon charge stock and in general is a lower-boiling hydrocarbon which is present initially in the heavy hydrocarbon charge stock or which is formed in carying out the process of this invention. In general the liquid material has a boiling point below 850°F. It is preferred that the liquid which is present in the second catalyst have at least 90% by weight of the liquid boiling below 850°F still more preferably at least 97% by weight and still more preferably at least 99% by weight boiling below 850°F.

The process of this invention can be utilized for the hydrodesulfurization and the hydrocracking of heavy hydrocarbon charge stocks. By the use f the term "hydrodesulfurization process" is meant that non-destructive hydrogenation takes place whereby the main effect of carrying out the process is to remove sulfur. In carrying out the process f this invention small or negligible amounts of lower-boiling hydrocarbons are obtained from the heavy hydrocarbon charge stock in a single pass, generally less than 15 wt. % 650°F+ conversion more preferably less than 5 wt. % 650°F+ conversion. Hydrocracking is herein defined to be destructive hydrogenation in which a substantial portion of the product boils at a temperature below that of the heavy hydrocarbon charge stock. In general percent conversions by weight per single pass of the 850°F+ material of the heavy hydrocarbon charge stock lies in the range of from 20 to 80% more preferably from 30 to 65%.

The hydrodesulfurization and hydrocracking conditions as to pressure, temperature and space velocity can be varied over a wide range, those conditions which are utilized being those which produce sulfur-removal in the one case and increased yield of lower-boiling hydrocarbons in the second case.

It is contemplated within the scope of this invention, that a catalyst present in the first and second catalyst zones under conditions of temperature and pressure can provide hydrodesulfurization whereas the same catalyst under different temperature and pressure conditions can provide hydrocracking of the heavy hydrocarbon material.

A wide variety of heavy hydrocarbon fractions and/or distillates can be used as a charge stock in the process of this invention. Such heavy hydrocarbon fractions include full-boiling-range crude oils, topped or reduced crude oils, atmospheric distillates, vacuum-tower bottoms, visbreaker bottoms product, heavy cycle stock from thermal or catalytically cracked charge stocks, and blends of two or more of the above charge stocks. A particularly preferred heavy hydrocarbon charge stock is the deasphalted atmospheric and vacuum-tower residues which have been topped to temperatures of at least 550°F at atmospheric pressure and those charge stocks and mixtures thereof which contain at least 10 wt. % 850°F+ hydrocarbon material more preferably about 25.

The first and second catalyst zone conditions that are utilized in the split-flow process of this invention are in general temperatures of from 600°F to 850°F, preferably from 725°F to 775°F for hydrodesulfurization and from 775°F to 825°F for hydrocracking; pressures of from 500 to 5000 psig, preferably from 1000 to about 2000 psig for hydrodesulfurization and from 1500 to 2500 psig for hydrocracking and liquid hourly space velocities of from 0.1 to 10, preferably from .2 to 1.5 for hydrodesulfurization and from .2 to 2.0 for hydrocracking volumes of feed per volume of catalyst per hour.

In general it is preferred to have approximately the same conditions in the first and second catalyst zone although the gas rates in the first and second catalyst zone will differ depending upon the amount of hydrogen which is blended together with the heavy hydrocarbon charge stock prior to the introduction into the catalyst zone and/or consumed in the process. Thus hydrogen gas rates in the second catalyst zone may be somewhat higher than the hydrogen rates in the first catalyst zone. In addition depending upon the percent conversion and/or desulfurization per single pass a different liquid hourly space velocity in the first and second catalyst zone can be used. In general the liquid hourly space velocity in the second catalyst zone will be greater than that in the first catalyst zone. In addition as in the case where the catalyst zones are not present in the same reactor, temperature and pressure can be varied.

The hydrodesulfurization catalysts comprise any of the transitional metals, metal oxides, metal sulfides, or other metal salts which are known to catalyse hydrodesulfurization, and are not poisoned by hydrogen sulfide or other sulfur compounds. The preferred catalysts comprise the oxides and/or sulfides, as for example the oxides or sulfides of molybdenum, tungsten, iron, cobalt, nickel, chromium and the like. Vanadium compounds may also be employed in some cases. A particularly active combination consists of a metal oxide or sulfide selected from chromium, molybdenum and tungsten with a group-VIII-metal oxide or sulfide. For example, compositions containing both molybdenum oxide and cobalt oxide, molybdenum oxide and nickel oxide, tungsten sulfide and nickel sulfide, may be employed.

A particularly active catalyst consists of the composite known as cobalt molybdate, which actually may be a mixture of cobalt and molybdenum oxides wherein the atomic ratio of Co to Mo may be between about 0.4 and 5.0. This catalyst, or any of the above catalysts may be employed in unsupported form, or alternatively it may be distended on a suitable adsorbent oxide carrier such as alumina, silica, zirconia, thoria, magnesia, titania, bauxite, acid-activated clays, or any combination of such materials.

The hydrocracking catalyst utilized for the conversion of the aforementioned hydrocarbon charge stocks can be alumino-silicate zeolite, having a platinum group metal (e.g. platinum or palladium) deposited thereon or composited therewith. These zeolites are characterised by their highly ordered crystalline structure and uniformly dimensioned pores, and have an alumino-silicate anionic cage structure wherein alumina and silica tetrahedra are intimately connected to each other so as to provide a large number of active sites, with the uniform pore openings facilitating entry of certain molecular structures. It has been found that alumino-silicate zeolites, having effective pore diameter of about 6 to 15, preferably 8 to 15 Angstrom units, when composited with the platinum group metal, and particularly after base exchange to reduce the alkali-metal-oxide (e.g. Na_2O) content of the zeolite to less than 10 wt. %, are effective hydrocracking catalysts, particularly for the hydrocarbon charge stocks herein contemplated.

In addition, the catalyst can be a supported hydrogenation catalyst comprising a Group VIII metal in the Periodic Table, such as nickel, cobalt, iron or one of the platinum group metals such as palladium, platinum, iridium, or ruthenium on a suitable support. Generally, it is preferred that an oxide or sulfide of a Group VIII metal (particularly iron, cobalt or nickel) be present in mixture with an oxide or sulfide of chromium, molybdenum or tungsten (preferably molybdenum or tungsten). Suitable carriers or supports include acidic supports such as: silica-alumina, silica-magnesia; the acidic clays; fluoride alumina; and mixtures of inorganic oxides, such as alumina, silica, zirconia, and titania, having sufficient acidic properties providing high cracking activity.

In addition the various metals and metal oxides and sulfides can be utilized on a mixture of support materials. Thus, for example, a zeolite and an alumina can be blended together as a support material in varying proportions which support materials contain various metals deposited thereon.

The invention can be better appreciated by the following non-limiting examples.

Example 1

To a 1500 cc split flow vertical pressure reactor equipped with charge-stock-inlet tube at the intermediate point in said reactor, effluent-exit tubes at the bottom and top of the reactor, a gas-inlet tube at the bottom of the reactor, a first and second fixed-screen catalyst bed containing 300 ccs. each of catalyst below and above the charge-stock-inlet tube respectively, each catalyst bed containing a nickel oxide (3 wt. %), molybdenum oxide (13.6 wt. %) on alumina (1/16" pellets) catalyst, and heating means is charged a Safaniya atmospheric reduced crude the properties of which are listed in Table 1 at a temperature of approximately 200°F in downflow relationship to the first hydrogenation catalyst bed at a space velocity of volumes of liquid per volume of catalyst per hour of 1.0. Hydrogen is introduced through the gas inlet tube in countercurrent relationship to the charge stock at a rate of 16,000 SCF per barrel liquid feed and a temperature of 775°F and a pressure of 1500 psig are maintained in the first and second catalyst beds. A product (effluent) is recovered from the first and second catalyst zones and combined.

Example 2

T a downflow reactor equipped with a charge stock and hydrogen-inlet tube and product-(effluent-) exit tube at the top and bottom of the reactor respectively utilizing a catalyst and charge stock as described in Example 1, is introduced hydrogen and the charge stock in downflow relationship to the catalyst at a liquid hourly space velocity of 1.0, a temperature of 775°F, a pressure of 1500 psig and a hydrogen gas rate of 16,000 SCF per barrel liquid feed. The product (effluent) is recovered.

Example 3

To a counter-flow-reactor equipped with charge-stock-inlet and gas-exit tubes at the top of the reactor and gas-inlet and effluent-exit tubes at the bottom of the reactor utilizing a catalyst and charge stock as described in Example 1, is introduced hydrogen and the charge stock in countercurrent relationship to the catalyst at a liquid hourly space velocity of 1.0, a temperature of 775°F, a pressure of 1500 psig and a hydrogen gas rate of 16,000 SCF per barrel liquid feed. The product (effluent) is recovered.

The analyses of the recovered product from Examples 1, 2 and 3 are given in Table 1 together with the properties of the charge stock.

TABLE I

Mode of Operation	Safaniya Reduced-Crude Charge Stock	Example 1 Counter-current Split Flow	Example 2 Downflow	Example 3 Counter-current
Product Recovery[1], wt. %				
$H_2S + NH_3$		.5	.4	.4
C_1		.3	.6	.2
C_3		.2	.5	.2
C_4's		.2	.6	.2
C_5's		.2	.8	.2
C_6—200°F } C_6—400°F		.4 } 12.2	.9 } 2.3	1.4
200°—400°F } C_6—400°F		11.8 } 12.2	1.4 } 2.3	
400°—650°F	1.5	26.5	6.3	14.0
650°—850°F	20.3	13.3	14.6	21.3
850°F +	78.2	46.3	73.4	61.9
Sulfur, wt. %	4.5	1.23	2.5	2.39
Desulfurization wt. %		72.7	44.5	46.9
850°F + conversion wt. %		40.3	6.2	20.8

[1]Hydrogen-free basis on total combined overhead and bottoms product.

Example 4

To a reactor as described in Example 1 wherein the first bed contains 300 ccs. of a nickel oxide (3 wt. %), molybdenum oxide (13.6 wt. %), on alumina (1/16") catalyst and the second catalyst bed contains a nickel oxide (6 wt. %) tungsten oxide (19 wt. %) on a support comprising 22% low-sodium zeolite, 56% silica and 20% alumina on a weight basis, is introduced an Arabian vacuum-reduced crude oil having the properties listed in Example 7 in downflow relationship to the first hydrogenation catalyst bed at a liquid hourly space velocity of 1.0. A temperature of 775°F, a pressure of 1500 psig and a hydrogen circulation rate of 18,000 SCF per barrel liquid feed are maintained in the first and second hydrogenation catalyst beds. A product boiling below 850°F is recovered from the second catalyst zone.

Example 5

To a reactor as described in Example 1 wherein the first bed contains 300 ccs. of a nickel sulfide (3.7 wt. %), molybdenum sulfide (18.1 wt. %) on alumina (1/16") catalyst and the second catalyst bed contains a nickel oxide (6 wt. %) tungsten oxide (19 wt. %) on a support comprising 22% low-sodium zeolite, 56% silica and 20% alumina on a weight basis, is introduced an Arabian vacuum-reduced crude oil having the properties listed in Example 7 in downflow relationship to the first hydrogenation catalyst bed at a liquid hourly space velocity of 1.0. A temperature of 775°F, a pressure of 1500 psig and a hydrogen circulation rate of 18,000 SCF per barrel liquid feed are maintained in the first and second hydrogenation catalyst beds. A product boiling below 850°F is recovered from the second catalyst zone.

Example 6

To a reactor as described in Example 1 wherein the first and second catalyst bed contain 300 ccs. each of a nickel oxide (6 wt. %) tungsten oxide (19 wt. %) on a support comprising 22% low sodium zeolite, 56% silica and 20% alumina on a weight basis, is introduced an Arabian vacuum-reduced crude oil having the properties listed in Example 7 in downflow relationship to the first hydrogenation catalyst bed at a liquid hourly space velocity of 1.0. A temperature of 775°F, a pressure of 1500 psig and a hydr gen circulation rate of 18,000 SCF per barrel liquid feed are maintained in the first and second hydrogenation-catalyst beds. A product boiling below 850°F is recovered from the second catalyst zone.

Example 7

To a reactor as described in Example 1 wherein the first and second catalyst bed contains 300 ccs. each of a nickel oxide (3 wt. %), molybdenum oxide (13.6 wt. %) on alumina (1/16") catalyst is introduced an Arabian Vacuum Reduced Crude having properties as follows:

Stock Name	*Arabina Vacuum-Reduced Crude*
°API	8.7
Carbon Residue, Wt. %	17.55
Sulfur, Wt. %	3.4
Nitrogen, Wt. %	.28
DPI Flask Dist., Wt. %	
IBP—400°F	—
400—650°F	—
650—850°F	—
850—EP	100

in downflow relationship to the first hydrogenation catalyst bed at a liquid hourly space velocity of 1.0. A temperature of 775°F, a pressure of 1500 psig and a hydrogen circulation rate of 17,500 SCF per barrel liquid feed are maintained in the first and second hydrogenation catalyst beds. A combined product is recovered from both the first and second catalyst zones.

Example 8

To a reactor as described in Example 1 wherein the first and second catalyst bed contain 300 ccs. each of a nickel oxide (3 wt. %), molybdenum oxide (13.6 wt. %) on alumina (1/16") catalyst is introduced an Arabian Vacuum-Reduced Crude having the properties listed in Example 7 in downflow relationship to the first hydrogenation catalyst bed at a liquid hourly space velocity of 1.0. A temperature of 775°F, a pressure of 1500 psig and a hydrogen circulation rate of 1600 SCF per barrel liquid feed are maintained in the first and second hydrogenation catalyst beds. A combined product is recovered from the first and second catalyst zones.

The properties of the combined product from Examples 7 and 8 are given in Table II.

TABLE II

	Product from Example 7	Product from Example 8
Hydrogen circulation rate	17,500 SCF/bbl.	1600 SCF/bbl.
Product Analysis		
Sulfur. Wt. %	1.22	2.09
Carbon residue Wt. %	7.93	12.52
Nitrogen, Wt. %	0.15	0.25
Desulfurization Wt. %	64.1	38.5

The results in Table I demonstrate the outstanding performance of the process of this invention for providing conversion of 850°F+ material on a single pass basis as compared to the countercurrent method of Example 2 and the downflow method of Example 3. In addition the desulfurization which is obtained under hydrocracking conditions is considerably in excess of that obtained by any of the two prior methods. Thus, in Example 1, a 40.3 wt. % conversion of 850°F+material was obtained which is 100 percent greater conversion than the countercurrent method and almost 700 percent greater conversion when compared to the downflow method. In addition, the desulfurization was twice that of the countercurrent and downflow methods. Of particular importance in demonstrating that liquid presence is essential in order to obtain optimum desulfurization are the results listed in Table II. More particularly, a comparison between Example 7 and Example 8 demonstrates a critical aspect of this invention that is, the maintaining of a lower-boiling liquid in the second catalyst zone. Thus, a comparison in hydrogen circulation rates of 17,500 SCF per barrel for the process of this invention and 1600 SCF per barrel gives a desulfurization by the process of this invention of 64.1 percent versus a desulfurization of 38.5. Thus the process of this invention provides for desulfurization almost twice as great as the prior-art method.

Example 9

San Ardo crude oil and a fluid-catalytic-cracker heavy cycle gas oil (FC HCGO) are blended in equal parts by volume to produce a charge stock.

Properties of these stocks are shown below:

	San Ardo Crude	FC HCGO
Gravity, °API	12.6	22.6
Carbon Residue, Wt. %	9.4	0.46
Sulfur, Wt. %	2.0	0.76
Nitrogen, Wt. %	0.82	0.8
Distillation, Wt. %		
Below 400°F	—	—
400—650°F	16.6	40.0
650—850°F	23.2	60.0
850—EP	60.1	—

To a reactor as described in Example 1 and containing catalysts as described in Example 4 is charged the above stock at a temperature of approximately 250°F in downflow relationship to the first catalyst zone at a space velocity of volumes of liquid per volume of catalyst per hour of 1.0. A hydrogen gas is introduced through the gas inlet tube in countercurrent relationship to the charge stock at a rate of 12,000 SCF per barrel liquid feed, and a temperature of 775°F and a pressure of 1500 psig are maintained in the first and second catalyst beds. Th entire hydrocarbon bottoms from the first catalyst bed is continuously recycled to the reactor in admixture with fresh charge stock resulting in a hydrocarbon bottom to fresh feed recycle rati on a volume basis of about 1.0. A product is recovered from the second catalyst zone through the effluent exit tube which has the following properties.

Inspection Data	Charge Stock	Recycle Bottoms	Product
Gravity, °API	17.2	13.0	27.0
Nitrogen, ppm	5810	8000	846
Sulfur, Wt. %	1.17	0.90	0.10
Carbon Residue, Wt. %	5.35	11.28	0.001
Hydrogen, Wt. %	11.2	10.5	12.0
Carbon, Wt. %	86.1	86.6	86.8

Yield Structure, Wt. %	Charge Stock	Recycle Bottoms	Product
Dry Gas	—	—	1.6
C_4's	0	0	0.4
C_5's	0	0	0.2
C_6 — 400°F	0.4	3.1	4.6
400—650°F	27.0	4.4	45.5
650—850°F	41.5	31.4	47.0
850°F +	31.1	61.1	0.6

Total conversion of 850°F+fraction is verified by analysis of samples of the bottoms recycle stream taken periodically during a 485 hour run which shows no appreciable build-up of carbon residue. Per-pass conversion of 850°F+components of the fresh feed stock is 33 weight percent and hydrogen consumption over a 48-hour period was 400 SCF per barrel of feed.

WHAT WE CLAIM IS:—

1. A hydrocarbon hydro-conversion process which comprises introducing a heavy hydrocarbon charge stock in downward flow into a reaction system in which the reaction conditions include a temperature of from 600 to 850°F and a pressure of from 500 to 5000 psig, said reaction system comprising a first catalyst zone below and a second catalyst zone above the point of entry of the heavy hydrocarbon charge stock, introducing hydrogen into said first catalyst zone in countercurrent relationship to said hydrocarbon charge stock in order to maintain a lower-boiling hydrocarbon liquid derived from the charge stock in the second catalyst zone and recovering lower-boiling hydrocarbons and/or hydrocarbons with reduced sulfur content.

2. A process as claimed in Claim 1, wherein lower-boiling hydrocarbons are recovered from the second catalyst zone.

3. A process as claimed in Claim 1 or 2, wherein a high-boiling effluent is recovered from the first catalyst zone and recycled to the hydrocarbon charge stock.

4. A process as claimed in Claims 1, 2 or 3, wherein hydrocarbons with reduced sulfur content are recovered from the first and second reaction zones.

5. A process as claimed in any preceding claim, wherein the lower-boiling liquid is maintained in the second catalyst zone by a hydrogen gas flow rate to the first catalyst zone of at least 3,000 SCF per barrel of hydrocarbon charge to the first catalyst zone.

6. A process as claimed in Claim 5, wherein the hydrogen gas rate is from 3,000 SCF per barrel to 25,000 SCF per barrel.

7. A process as claimed in any preceding claim, wherein the lower-boiling hydrocarbon liquid has at least 97% by weight boiling below 850°F.

8. A process as claimed in any preceding claim, wherein the lower-boiling hydrocarbon liquid has at least 99% by weight boiling below 850°F.

9. A process as claimed in any preceding claim, wherein the hydrogen-gas-flow rate in the second catalyst zone is higher than the flow rate in the first catalyst zone.

10. A process as claimed in any preceding claim, wherein the reaction conditions include a temperature of from 725 to 775°F and a pressure of 1000 to 2000 p.s.i.g.

11. A process as claimed in any preceding claim, wherein the reaction conditions include a temperature of from 775 to 825°F and a pressure of 1500 to 2500 p.s.i.g.

12. A process of hydrocarbon hydro-conversion as claimed in Claim 1, and substantially as hereinbefore described with reference to Examples 1, 4, 5, 6 and 7 or 9.

13. The products of the process claimed in any of the preceding claims.

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